65

ELECTRONIC SPECTRA OF *o*-CHLOROPHENOL IN DIFFERENT ENVIRONMENTS AND AT DIFFERENT TEMPERATURES*

S. B. ROY

OPTICS DEPARTMENT, INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE, JADAVPUR, CALCUTTA-32

(*Received for publication, September* 19, 1958)

ABSTRACT. Investigations have been carried out on the ultraviolet absorption spectra of pure *o*-chlorophenol and its solutions in CCl_4, cyclohexane, 3-methyl pentane and isobutyl alcohol at different temperatures. Both the pure liquid and .01% solution in CCl_4 show band systems with the 0,0 band at 35475 cm^{-1}, the bands in the former case being much broader. From a comparison of these spectra with those due to the vapour it has been concluded that some of the molecules in the pure liquid and most of the molecules in the solution are of trans configuration. Broadening of the bands in the spectrum due to pure liquid is ascribed to the presence of dimers in the liquid.

The spectra due to .01% solution in 3-methylpentane or cyclohexane are found to consist of a strong system of bands accompanied by a much weaker system displaced from the former towards higher energies by 346 cm^{-1} The stronger system has been assigned to trans molecules and the weaker one to molecules which form H-Cl bonds with neighbouring solvent molecules

The spectrum due to .01% solution in isobutyl alcohol shows a band system shifted towards longer wavelengths with respect to that in the case of the pure liquid by about 400 cm^{-1}. This unusually large shift towards red has been accounted for by assuming a strong interaction between solvent and solute molecules resulting in the formation of a compound similar to a trisubstituted benzene compound.

INTRODUCTION

It was first pointed out by Pauling (1936) that the two peaks at 6910 cm^{-1} and 7050 cm^{-1} observed by Wulf and Liddel (1935) in the infra red spectrum of solution of *o*-chlorophenol in CCl_4, might be due to the first harmonic of O-H valence oscillation in the cis and the trans configuration respectively. Later, Davies (1938) in repeating the same investigation in the region of 3450-3600 cm^{-1} at different temperature, supported the hypothesis of Pauling.

Errera and Mollet (1935) observed a broad absorption peak with a maximum at 6620 cm^{-1} in the infra red spectrum of the pure liquid. Pauling (1945) interpreted the result by suggesting that the further lowering of O-H frequency even below 6910 cm^{-1}, might be due to formation of dimers in which

* Communicated by Prof. S. C Sirkar,

the hydrogen atom of the O-H group in the trans molecule is linked with the oxygen atom of O-H group in the cis molecules in the liquid.

W. Lüttke and R. Mecke (1950) also investigated the infrared spectrum of *o*-chlorophenol in solution of CCl_4 in the region of 10000–10500 cm^{-1} and reported that the strong band at 10090 cm^{-1} and weak band at 10325 cm^{-1} are due to second harmonic of the O-H valence oscillation in the cis and the trans form respectively. These frequencies are not one and half times of those reported by Wulf and Liddel (1935).

Recently. Sirkar *et al* (1958) investigated the infrared spectrum of *o*-chlorophenol in the liquid state and its solution in CCl_4 and cyclohexane at various concentrations and temperatures in the region 3000-3700 cm^{-1}. They reported that the broad absorption bands due to *o*-chlorophenol in the pure liquid might be produced by the superposition of the three main broad bands at 3320, 3450 and 3500 cm^{-1} with a small inflexion at 3620 cm^{-1} They ascribed the first peak to dimers as proposed by Pauling and the second one at 3450 cm^{-1} to the cis molecules. From the spectrum due to 5% solution of *o*-chlorophenol in CCl_4, Sirkar *et al* concluded that the strong absorption peak at 3533 cm^{-1} is due to the O-H valence oscillation in trans molecules and suggested that 3595 cm^{-1} might be due to a combination frequency

From an investigation of the Raman spectra of solutions of *o*-chlorophenol in different solvents Mukherjee (1958) reported that the intensity of O-H line 3533 cm^{-1} increases with decrease of concentration of the solution. He concluded that the molecules of trans configuration become predominant in weak solution.

It is well known that the ultraviolet absorption spectra of substituted benzenes are affected appreciably by environment (Roy, 1956). It would, therefore, be interesting to study the influence of environment on the ultraviolet absorption spectrum of the ortho chlorophenol molecule. The object of the present investigation was to study such spectra of solutions of *o*-chlorophenol in different solvents in the liquid and solid states with a view to finding out whether the data furnished any information regarding the configuration of the molecule in the state of aggregation. The results discussed in the later sections show that different solvents have influences of different nature on the absorption spectra of the molecule.

EXPERIMENTAL

The experimental arrangement is similar to that described in an earlier paper (Roy, 1956). The solvents used were CCl_4, cyclohexane, 3-methyl pentane and isobutyl alcohol. The latter two solvents form rigid glass at $-180°C$. All the solvents were found to have no absorption in the region under consideration. *o*-Chlorophenol obtained from B.D.H. was of chemically pure quality. It was fractionated and the proper fraction was redistilled under reduced pressure.

The spectra were photographed on Ilford HP3 films with a Hilger medium quartz spectrograph. Iron arc spectrum was taken on each film as a comparison. Microphotometric records were taken with a Kipp and Zonen type microphotometer. The absorption spectra were calibrated with the help of microphotometric records of iron lines using the method described earlier (Roy, 1956).

RESULTS AND DISCUSSION

The microphotometric records of the absorption spectra of *o*-chlorophenol in the liquid and the solid state and its solution in CCl_4 are given in figure 1; those of

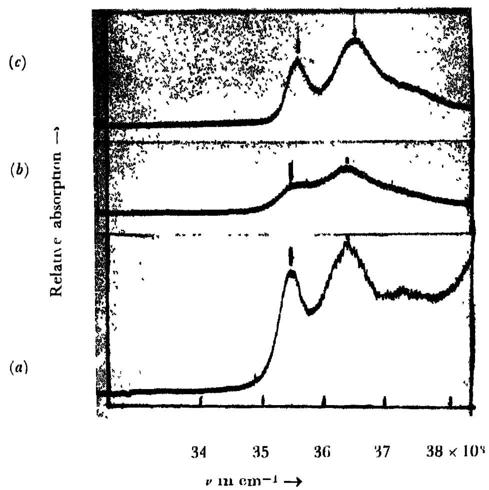

Fig. 1. Microphotometric records of absorption spectra of *o*-chlorophenol
(*a*) 01% solution in CCl_4 with 5 mm cell at 30°C
(*b*) Pure liquid at 30°C
(*c*) Pure solid at −180°C

the solutions in cyclohexane, 3-methyl pentane and isobutyl alcohol are given in figures 2 and 3. The frequencies of the absorption bands and their probable assignments are given in Tables 1, II and III. The data for the gaseous state (Ramasastri, 1951) are included in Table I for comparison

It can be seen from figure 1(a) that the spectrum due to .01% solution of *o*-chlorophenol in CCl_4 consists of three sharp bands with the 0, 0 band at 35475 cm^{-1} and excited state vibration frequency 917 cm^{-1}, whereas in the vapour state the 0, 0 band is at 35892 cm^{-1} and the corresponding excited state frequency is 953 cm^{-1}. So the solvent produces a shift of the band system to lower energies of about 417 cm^{-1} and slight lowering of excited state frequency. The pure liquid shows much broader bands with their centres in the same positions as in the spectrum due to the solution in carbon tetrachloride. It is thus evident that the cause of this lowering of excited state energy of the molecule is the same in both the cases. Only chlorine atom is common in both the carbon tetrachloride molecule and *o*-chlorophenol molecule and probably the influence of the chlorine atom of a neighbouring molecule is responsible for this shift of the 0, 0 band. In that case it appears that the chlorine atom of the *o*-chlorophenol molecule in the liquid state is free to form some sort of linkage with the hydrogen atom of the benzene ring in the neighbouring molecule and in the solution in CCl_4, the chlorine atom of the solvent molecule may form such linkages with the hydrogen atom of benzene ring of the *o*-chlorophenol molecule.

In the solution each molecule of the solute is surrounded by large number of atoms of the solvent molecules and therefore there is higher probability of more than one C-H group being under the influence of surrounding chlorine atoms than in the pure liquid If such an influence in the solution on more than one C-H group would shift the 0, 0 band to 35475 cm^{-1}, only a fraction of the total number of the molecules may be under such an influence in the pure liquid and in the rest only one CH group may be under the influence of the chlorine atom of a neighbouring molecule. The shift of the 0, 0 band in the case of these latter molecules from its position in the spectrum due to vapour is expected to be smaller. The position of the broad 0. 0 band on the shorter wavelength side of 35475 cm^{-1} may be produced by these latter molecules and also by the dimers which may be present in the liquid (Pauling, 1945)

Thus it can be concluded from these results that in the pure liquid some of the molecules have the chlorine atom free from the influence of the O-H group and these molecules are of the trans configuration. Hence it can be seen from the above arguments that in the solution in carbon tetrachloride most of the molecules of the solute have the trans configuration. This conclusion is in agreement with those arrived at by Sirkar *et al* (1958) from the results of the investigation on the infrared absorption spectra of solutions of *o*-chlorophenol.

The spectrum due to pure solid at $-180°C$ (figure1 c), however, consists of three bands which are slightly sharper than that due to pure liquid and the 0, 0 band at 35600 cm^{-1}, is shifted towards shorter wavelength from the main peak at 35475 cm^{-1} in the spectrum due to pure liquid. This main peak is due to the molecules in which more than one CH group are under the influence of chlorine atom of the neighbouring molecules and the portion on the shorter wavelength side of the band at 35475 cm^{-1} has been assigned to those molecules in which only one CH group has been affected by the chlorine atom of the neighbouring molecule. So it appears that in the solid state the number of latter molecules increases and the number of those molecules in which more than one

CH group are affected, diminishes. If the position of the broad band due to the liquid further away from 35475 cm^{-1} towards shorter wavelength be assigned to dimers in which O–H–O is formed between two molecules, it appears that the number of such molecules in the solid state is much smaller because the absorption in this region in the solid state is very small.

Figure 2(a) shows that in the spectrum due to solution of orthochlorophenol in 3-methyl pentane in addition to three strong bands, as in the case of solution in CCl_4, three other weaker bands appear and the 0, 0 band at 35640 cm^{-1} is shifted

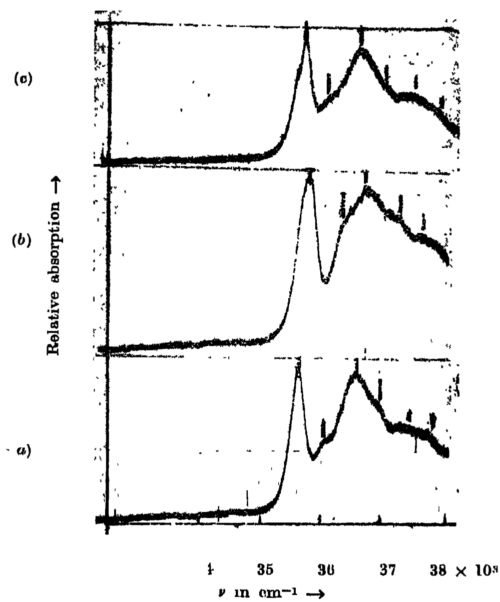

Fig. 2. Microphotometric records of the absorption spectra of o-chlorophenol.
(*a*) .01% solution in 3 methyl pentane with 5 mm cell at 30°C.
(*b*) .01% solution in 3 methyl pentane with 5 mm cell at −180°C.
(*c*) .01% solution in cyclohexane with 5 mm cell at 30°C.

towards higher energy by 165 cm^{-1} with respect to that due to the liquid. This shift can be explained by assuming that as the chlorine atom is surrounded by large number of hydrogen atoms in the solvent molecules, the O-H group is set free and the molecules assume trans configuration. If in some of these molecules the chlorine atom would form a virtual bond with the hydrogen atom of the solvent molecule, the migration effect would be reduced and the band system would shift to higher energies. The weak band at 35986 $cm^{-1}$and the other two such bands on the shorter wavelength side may be due to these molecules. It is seen from figure 2(b) that when solution is frozen and cooled to $-180°C$, the intensity of the weaker band system increases and the bands are shifted towards higher energies. This is expected according to the hypothesis mentioned above, because at lower temperature, the distance between molecules diminishes and the probability of H–Cl bond formation increases and also the strength of the bond is expected to increase at closer distances.

TABLE I

Absorption spectra of *o*-chlorophenol

Vapour (Ramasastri, 1951) Prominent bands		Liquid at 28°C		Solid at −180°C		.01% sol. in CCl_4 (liquid at 28°C)	
ν in cm^{-1}	Assignment	ν in cm^{-1}	ment	ν in cm^{-1}	Assignment	ν in cm^{-1}	ment
35892 (vs)	ν_0	35475 (b)	ν_0	35600 (s)	ν_0	35475 (s)	ν_0
36387 (w)	ν_0+495	36392 (b)	ν_0+917	36512 (s)	ν_0+912	36392 ((s)	ν_0+917
36527 (m)	ν_0+635	37310 (b)	$\nu_0+2\times917$	37426 (w)	$\nu_0+2\times912$	37310 (w)	$\nu_0+2\times917$
36693 (m)	ν_0+801						
36845 (s)	ν_0+953						
36982 (m)	ν_0+1090						
37092 (w)	ν_0+1200						
37377 (vw)	ν_0+1485						

TABLE II

Absorption spectra of *o*-chlorophenol

.01% sol. in 3-methyl pentane (liq. at 28°C)		.01% sol. of 3-methyl pentane (solid at −180°C.)		.01% sol. in cyclohexane (liquid at 28°C)	
ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment	ν in cm^{-1}	
35640 (s)	ν_0	35767 (s)	ν_0	35729 (s)	ν_0
35986 (w)	ν_0'	36286 (m)	ν_0'	36079 (w)	ν_0'
36552 (s)	ν_0+912	36672 (s)	ν_0+905	36645 (s)	ν_0+916
36903 (w)	$\nu_0'+912$	37191 (m)	$\nu_0'+905$	36998 (w)	$\nu_0'+916$
37470 (m)	$\nu_0+2\times912$	37580 (w)	$\nu_0+905\times2$	37556 (w)	$\nu_0+916\times2$
				37917(vw)	$\nu_0'+916\times2$

TABLE III

Absorption spectra of *o*-chlorophenol

.01% sol. in isobutyl alcohol (liq. at 28°C)		.01% sol. in isobutyl alcohol (solid at −180°C)		20% sol. in isobutyl alcohol (liq. at 28°C)		20% sol. in isobutyl alcohol (solid at −180°C)	
ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment
35065 (m)	ν_0	35065 (m)	ν_0	35488 (b)	ν_0	35475	ν_0
35241 (s)	ν_0'	35241 (s)	ν_0'	36405 (b)	ν_0+917	36392	ν_0+917
35488 (m)	ν_0''	35488 (m)	ν_0''	37329 (b)	$\nu_0+917\times 2$	37316	$\nu_0+917\times 2$
35985 (s)	ν_0+920	35985 (s)	ν_0+920				
36168 (s)	$\nu_0'+917$	36168 (s)	$\nu_0'+917$				
36405 (m)	$\nu_0''+917$	36401 (m)	$\nu_0''+917$				
36902 (w)	$\nu_0+2\times 917$	36902 (w)	$\nu_0+2\times 917$				
37094 (w)	$\nu_0'+2\times 917$	37094 (w)	$\nu_0'+2\times 917$				
37329 (vw)	$\nu_0''+2\times 917$	37329 (vw)	$\nu_0''+2\times 917$				

Similar results are also observed in the case of solution of *o*-chlorophenol in cyclohexane at room temperature.

It can be seen from figure 3(d) Table III that the 0,0 band in the spectrum due to .01% solution of *o*-chlorophenol in isobutyl alcohol at room temperature is shifted towards longer wavelengths even with respect to the 0, 0 band due to the pure liquid by about 410 cm^{-1}. This large shift towards red suggests that some strong interaction takes place between *o*-chlorophenol and isobutyl alcohol molecules. Strong interaction between *o*-chlorophenol and alcohol molecules was also reported by Rene Freymann (1940) from the intensity of .99μ band in the infrared absorption spectrum of solution of *o*-chlorophenol in alcohols. It is evident from the amount of shift of the band system that the interaction between *o*-chlorophenol molecule and isobutyl alcohol molecules is different from that between *o*-chlorophenol in methyl pentane or cyclohexane. In this case formation of some new types of bonds between O–H group of alcohol and hydrogen atom of CH group of chlorophenol may take place, and thereby a trisubstituted benzene-like compound is produced. This explanation is supported by the fact that the calculated position of the 0, 0 band at 35130 cm^{-1} in the spectrum due to pure 1, 3, 5-trichlorobenzene in the liquid state is near to the band at 35065 cm^{-1} in the spectrum due to .01% solution of *o*-chlorophenol in the liquid state. The spectrum due to frozen .01% solution of *o*-chlorophenol in isobutyl alcohol is similar to that due to same solution in liquid state, but bands become sharper at the lower temperature.

The spectrum due to 20% solution of o-chlorophenol in isobutyl alcohol is similar to that of the pure substance, only with slight shift towards longer

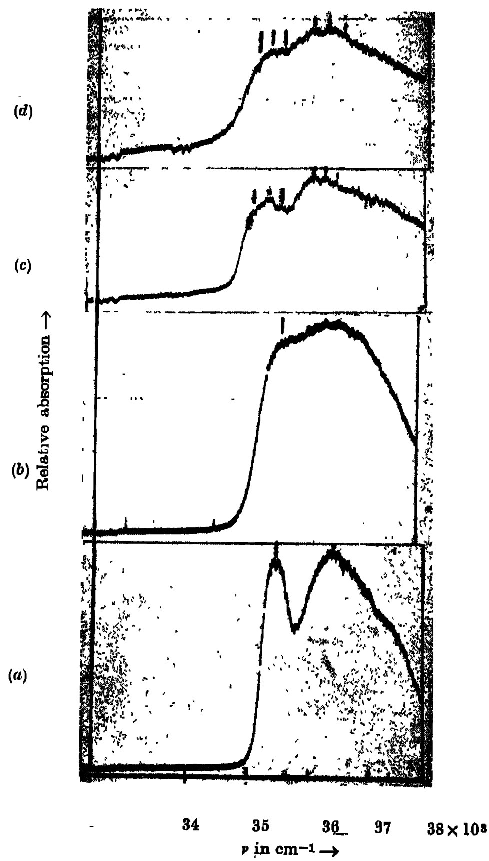

Fig. 3. Microphotometric records of the absorption spectra of o-chlorophenol.
(a) 20% solution in isobutyl alcohol at −180°C.
(b) ,, ,, ,, ,, ,, ,, 30°C.
(c) .01% ,, ,, ,, ,, ,, −180°C.
(d) ,, ,, ,, ,, ,, ,, 30°C.

wavelength. So, as in the case of pure liquid most of the *o*-chlorophenol molecules in 20% solution remain in groups and give spectrum like that of the pure substance.

ACKNOWLEDGMENT

The author is indebted to Professor S. C. Sirkar, D.Sc. F. N.I., for his kind help and guidance during the progress of this work.

REFERENCES

Davies, M. M., 1938, *Trans. Farad. Soc.*, **34**, 1427.
Errera, J. and Mollet, P., 1935, *Jour de Physique*, **6**, 281.
Lüttke, W. and Mecke, R., 1950, *Zeit. Phys. Chem.*, **196**, 56.
Mukherjee, D. K., 1958, *Ind. J. Phys.*, **32**, 192.
Pauling, L., 1936, *J. A. C. S.*, **58**, 94.
" 1945, Nature of Chemical Bond, p. 324.
Ramasastri, C., 1951, *Proc. Nat. Ins. Sc.* (Ind.), **17**, 349.
Rene Freymann, 1940, *Comp. Rend.*, **211**, 386.
Roy, S. B., 1956, *Ind. J. Phys.*, **30**, 267.
Sirkar, S. C., Deb. A. R. and Banerjee, S. B., 1958, *Ind. J. Phys.*, **32**, 345.
Wulf, O. R. and Liddel, U., 1935, *J. A. C. S.*, **57**, 1464